Supplementary Material (ESI) for Green Chemistry

ESI:

Synthesis and Characterisation of the Sn-H networks:

a) Synthesis of phenyltin derived networks

Typically, Mg (0.29g, 12mmol), a PTFE stirrer bar and some anti-bumping granules were dried in a Shlenk flask in an oven. The hot apparatus was constructed under a purge of N_2 gas, to the still hot Mg, a small I_2 crystal was added and the vapours allowed to accumulate in the Shlenk thereby activating the surface of the Mg turnings. Approximately 2 ml of a solution of 1,12-dibromododecane (1.83g, 5.6mmol) in freshly distilled dry degassed diethyl ether (10ml) was added to the Mg, this was stirred immediately and reactions became white and warmed always within about 1 min. The remaining dihalide was slowly added keeping the solutions warm after which the diGrignard was stirred for a further 1h at room temperature. The diGrignard reagent was added to $PhSnCl_3$ (0.675g, 2.23mmol) in freshly distilled dry degassed diethyl ether (2-3ml), the networks formed immediately as white rubbery solids that were generally heated under reflux for 24h. The excess Grignard functions were hydrolysed with a solution of saturated NH_4Cl (approx 25ml) and the air stable solid recovered by filtration and washing with water and diethyl ether. The networks were dried under vacuum at 110°C before washing in 2M HCl (10ml)/diethyl ether (10ml) followed by filtration and washing with water and diethyl ether. The networks were finally dried under vacuum at 110°C

b) Synthesis of tin bromide and in-situ generation of tin hydride networks

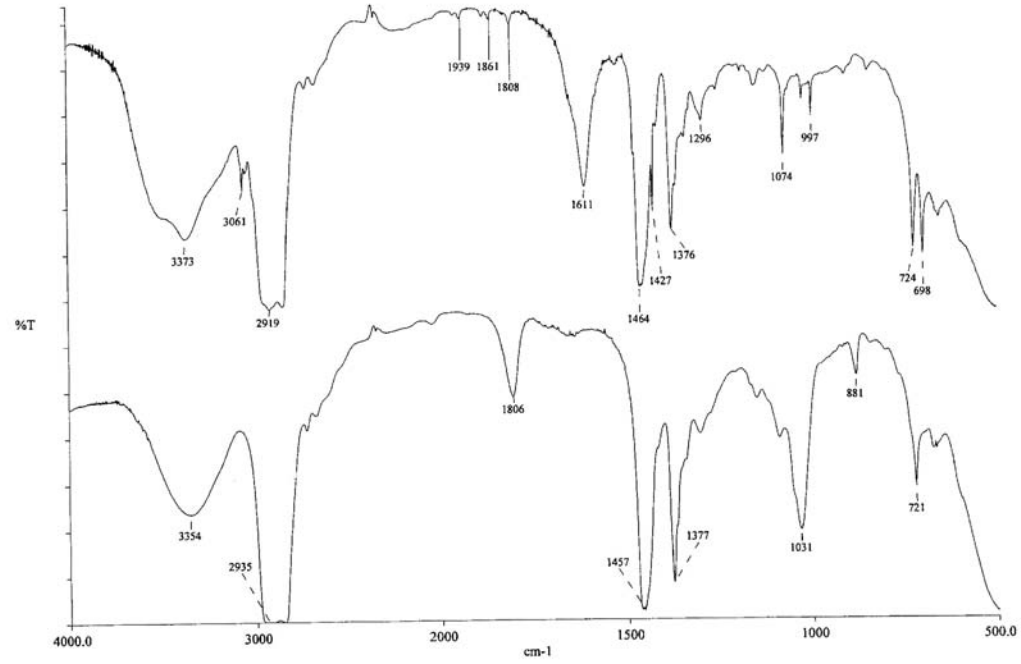
Typically, the phenyltin derived network (400mg, 0.65mmol of Sn) would be swollen in diethyl ether and Br_2 (104mg, 0.65mmol) added at room temperature, once the solution had lost its colouration the networks were washed with ether and this ether evaporated to dryness and weighed. The networks were treated with an excess of $NaBH_4$ in ethanol at 80°C for 6h, after which the networks were extensively washed with MeOH (4 x 10ml) and 1-butanol (2 x 10ml).

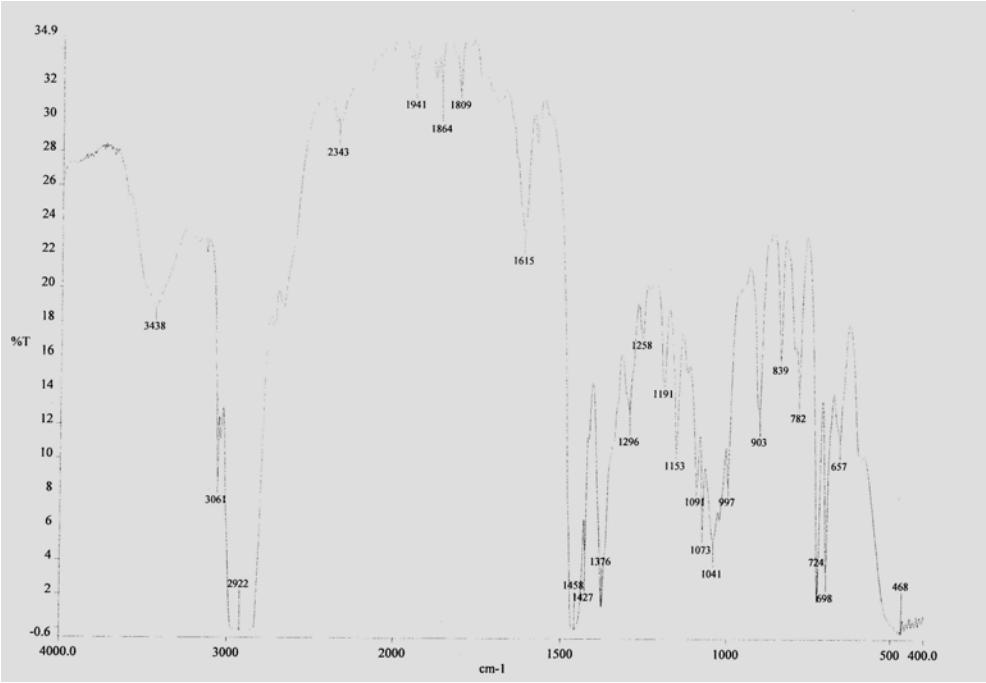
c) Determination of the active tin hydride content

To the *in-situ* prepared network of tin hydride, 1-butanol (10ml), an AIBN crystal (1-2 mol%) and 1-iodooctane (266mg, 1.1mmol) were added and the solution heated to 80°C for 6h, after cooling the solution was removed and the glassware and network washed with approximately another 10ml 1-butanol. The conversions to n-octane were evaluated by G.C.

d) FT-IR transmittance spectra of phenyl derivative (above) and Sn-H networks (below), respectively.

It is noted that the characteristic Sn-H peak (ν= 1806 cm^{-1}) is clearly evident in the Sn-H networks which also showed some residue butanol (ν_{C-O} = 1031 cm^{-1})





A control experiment of the direct phenyltin chloride and $NaBH_4$, an extremely small peak is found at the characteristic Sn-H region (ν ~1864 cm^{-1}).

e) A small soluble network fragments in $CDCl_3$ was prepared under dilute conditions for NMR characterisations:

$\underline{PhSn((CH_2)_{12})_{3/2}}$ *as* $\underline{H^dC(CH^e)_2(CH^f)_2CSn(CH^a{}_2CH^b{}_2(CH^c{}_2)_8CH^b{}_2CH^a{}_2)_{3/2}}$
(H^a, 1.5, m6 (s observed)), (H^b and H^c, 1.1, m9 and m5 (messy)), (Terminal CH_3 groups, 0.8, t), (R-CH_2-CH_3, 0.95, m12 (messy)), (H^d and H^e, 7.2, m), (H^f, 7.35, m), ($CHCl_3$, 7.2, s).

Table 1 ^{1}H NMR spectral assignments for $PhSn((CH_2)_{12})_{3/2}$

Assignment	Shift As ppm	Multiplicity & Comments
H^a, Sn-C**H**$_2$	1.5	M6, observed as singlet
H^b, Sn-CH$_2$C**H**$_2$	1.55	M9, observed as singlet
H^c, Sn-CH$_2$CH$_2$(C**H**$_2$)$_8$	1.30	M5, observed as singlet
Terminal C**H**$_3$ groups	0.87	Triplet
R-C**H**$_2$-CH$_3$	0.95	M12 (messy)
Aromatic **H**^{d} and **H**^{e}	7.30	Multiplet
Aromatic **H**^{f}	7.45	Multiplet
C**H**Cl$_3$	7.25	NMR solvent, singlet

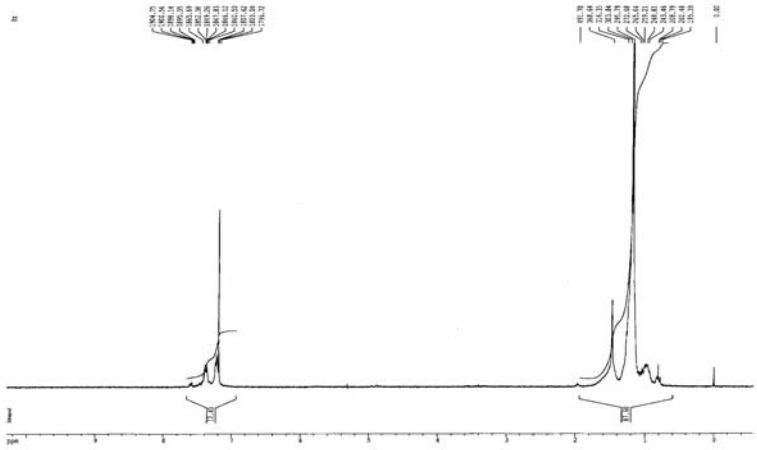


Figure 1 ^{1}H NMR spectrum of PhSn((CH$_2$)$_{12}$)$_{3/2}$

PhSn((CH$_2$)$_{12}$)$_{3/2}$

(Aromatic carbon bonded to Sn, 136.5, s), (Aromatic carbons, 128.6, s x 3), (**C**DCl$_3$, 77.1, q), (diethyl ether CH$_3$**C**H$_2$O, 65.9), (Sn(CH$_2$)$_2$**C**H$_2$, 34.4-33.9), (alkyl-**C**H$_2$CH$_2$CH$_3$, 32.0, 31.6), (Sn(CH$_2$)$_3$(**C**H$_2$)$_6$, 29.7-29.3), (alkyl-**C**H$_2$(CH$_2$)$_2$CH$_3$, 29.1), (SnCH$_2$**C**H$_2$, 26.9-26.7), (unknown, 26.0-25.5), (alkyl-**C**H$_2$CH$_3$, 22.7, s), (diethyl ether **C**H$_3$, 15.3), (Terminal **C**H$_3$ groups, 14.2, s), (Sn**C**H$_2$, 9.9).

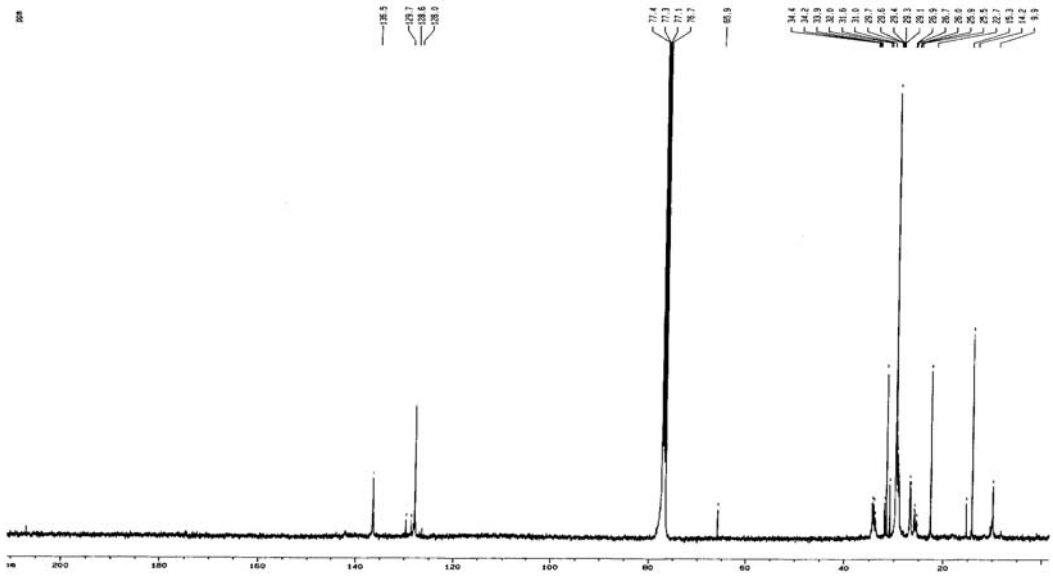


Figure 2 ^{13}C NMR spectrum of PhSn((CH$_2$)$_{12}$)$_{3/2}$.

Table 2: $BrSn((CH_2)_{12})_{3/2}$ $BrSn(CH^a{}_2CH^b{}_2(CH^c{}_2)_8CH^b{}_2CH^a{}_2)_{3/2}$

Assignment	Shift As ppm	Multiplicity & Comments
$Sn(CH_2)_{11}C\mathbf{H}_2Br$	3.58	t, small
H^a, Sn-$C\mathbf{H}_2$	1.58 to 1.61	Messy multipet
$Sn(CH_2)_{10}C\mathbf{H}_2CH_2Br$	1.85	Multiplet, small
H^b, Sn-$CH_2C\mathbf{H}_2$	1.27	Side peak on H^c
H^c, Sn-$CH_2CH_2(C\mathbf{H}_2)_8$	1.19	m
Terminal $C\mathbf{H}_3$ groups	0.78, 0.81, 0.84	t
Aromatic **H**'s	7.50 to 7.20	Trace amount of Sn-**Ph**
$C\mathbf{H}Cl_3$	7.20	s

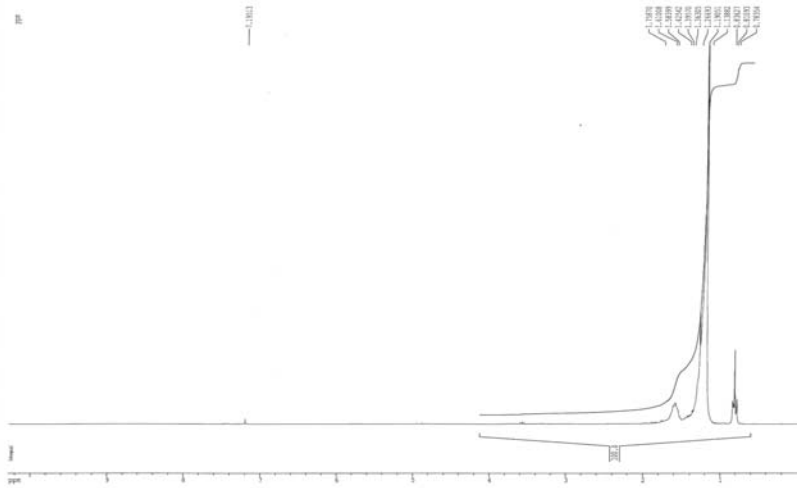


Figure 3 ^{1}H NMR spectrum of $BrSn((CH_2)_{12})_{3/2}$.

$BrSn((CH_2)_{12})_{3/2}$

($\mathbf{C}DCl_3$, 77.9, 77.4, 76.9, t), ($\mathbf{C}H_2Br$, 33.9), ($\mathbf{C}H_2CH_2Br$, 34.1), ($\mathbf{C}H_2CH_2CH_2Br$, 29.4), ($\mathbf{C}H_2CH_2CH_3$, 32.34, s), ($SnCH_2CH_2\mathbf{C}H_2$, 31.8, s), ($SnCH_2CH_2CH_2(\mathbf{C}H_2)_6$ and $\mathbf{C}H_2CH_2CH_2CH_3$, 30.1 to 29.6), ($SnCH_2\mathbf{C}H_2$, 26.5 to 25.6, s), (unknown , 24.0) ($\mathbf{C}H_2CH_3$, 23.1, s), ($Sn\mathbf{C}H_2$, 18.9 to 18.1), (Terminal $\mathbf{C}H_3$, 14.5, s).

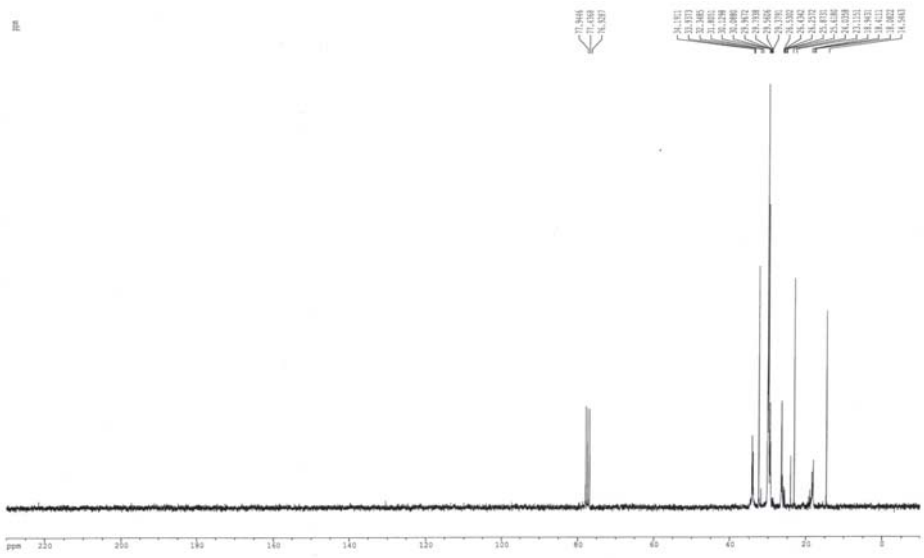


Figure 4 Carbon-13 NMR spectrum of $BrSn((CH_2)_{12})_{3/2}$.

$HSn((CH_2)_{12})_{3/2}$ as $H^dSn(CH^a{}_2CH^b{}_2(CH^c{}_2)_8CH^b{}_2CH^a{}_2)_{3/2}$

($CHCl_3$, 7.19, s), (H^d, 5.221, 5.216, 5.211, t), (H^a, 1.60, m), (H^b, 1.45, m), (H^c, 1.22, m), (terminal CH_3 groups, 0.81, t).

Table 3 ^{1}H NMR spectral assignments for $HSn((CH_2)_{12})_{3/2}$

Assignment	Shift As ppm	Multiplicity & Comments
H^a, Sn-C**H**$_2$	1.60	m
H^b, Sn-CH_2C**H**$_2$	1.45	m
H^c, Sn-CH_2CH_2(C**H**$_2$)$_8$	1.22	m
Terminal C**H**$_3$ groups	0.81	Triplet
Sn-**H**^{d}	5.221, 5.216, 5.211	Triplet
$CHCl_3$	7.19	Singlet
Aromatic **H**'s	7.70 to 7.30	M, trace amount

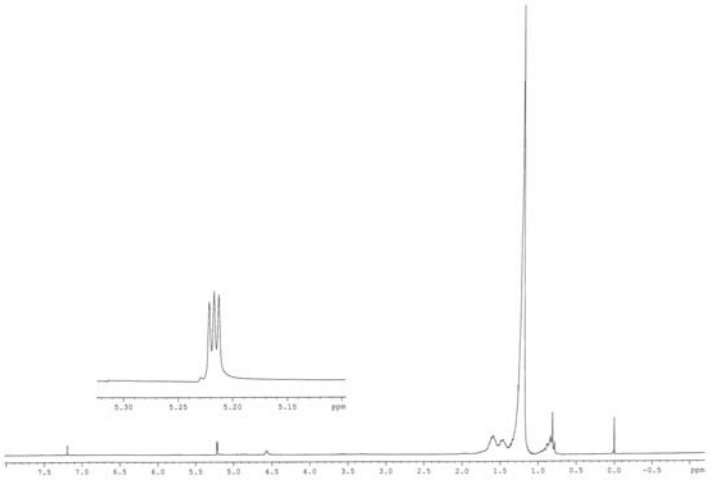


Figure 5 ^{1}H NMR spectrum of $HSn((CH_2)_{12})_{3/2}$.

<u>$HSn((CH_2)_{12})_{3/2}$</u>

(**C**DCl_3, 78.0, 77.4, 76.8, t), ($SnCH_2CH_2$**C**H_2, 34.8-33.9), (**C**$H_2CH_2CH_3$, 32.34, s), ((alkyl)$_3$SnSnCH_2CH_2**C**H_2 from air exposure, 31.8), (Sn$(CH_2)_3$(**C**$H_2)_6$, 30.5-29.1), (**C**$H_2CH_2CH_2CH_3$, 29.8, s), ((alkyl)$_3$SnSnCH_2**C**H_2 from air exposure, 28.2-27.6), ($SnCH_2$**C**H_2, 26.5-25.7), ($SnCH_2CH_2CH_2$(**C**$H_2)_6$, 30.5 to 26.1), (**C**H_2CH_3, 23.1, s), (Sn**C**H_2, 17.8-17.2), (Terminal **C**H_3, 14.5, s) ((alkyl)$_3$SnSn**C**H_2 from air exposure, 8.89).

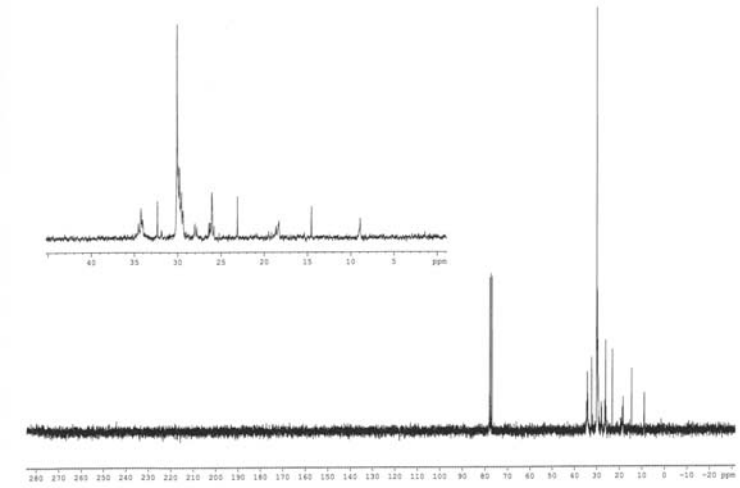
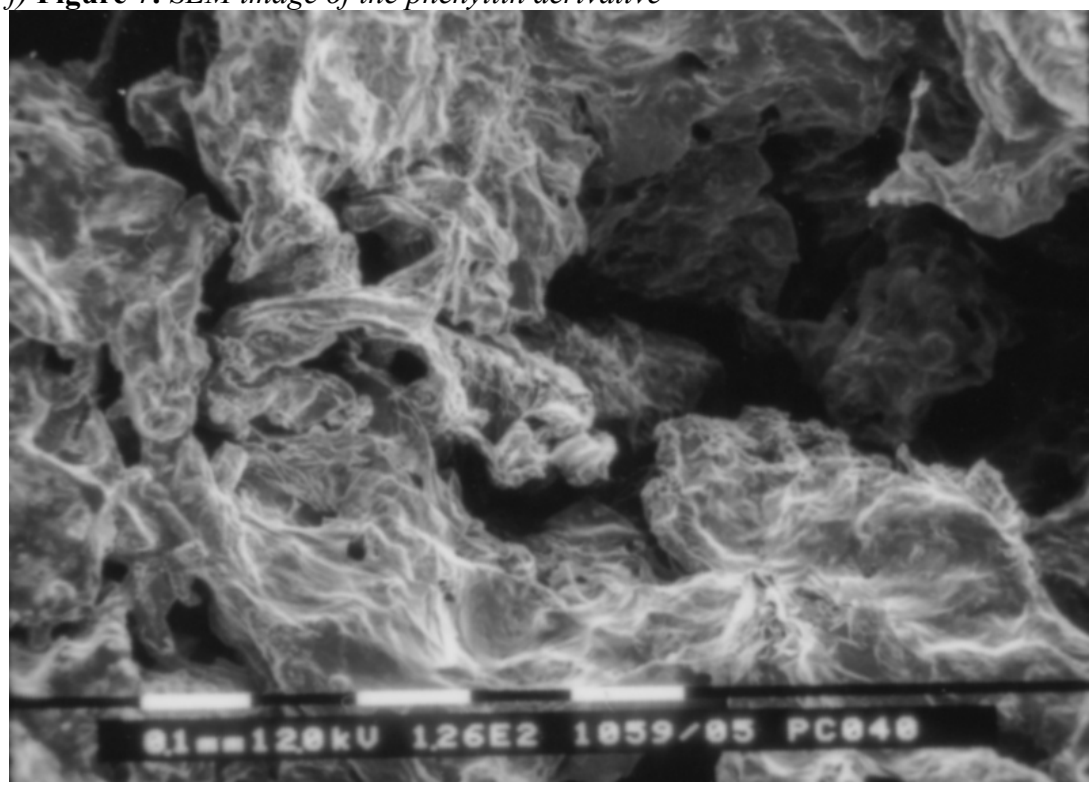


Figure 6 Carbon-13 NMR spectrum of $HSn((CH_2)_{12})_{3/2}$.

f) **Figure 7:** *SEM image of the phenyltin derivative*



g) Model Reactions

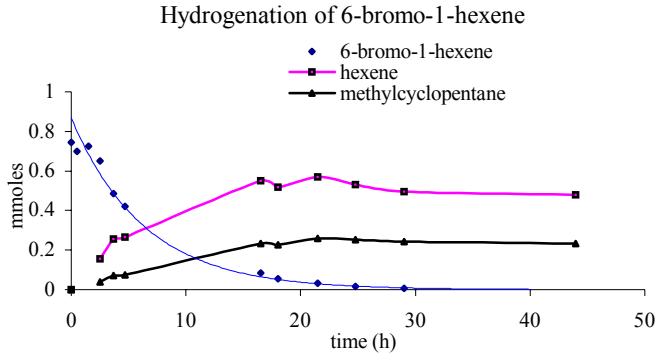
In order to demonstrate that the Sn-H network can be used as a substitute for soluble trialkyl Sn-H model synthetic reactions are established and compared with this conventional soluble reagent.

(i) ***Reduction of 6-bromo-1-hexene to methylcyclopentane (MCP)***

Experimental (MCP selectivity)

The selectivity of the free radical reduction of 6-bromo-1-hexene to methylcyclopentane (MCP) and hexene was studied. Approximately 1 g of previously used polymeric network in the form of the SnI ($ISn((CH_2)_{12})_{3/2}$) was regenerated to the tin hydride with diisobutylaluminium hydride (20 wt % in toluene, used in excess) and washed with water and toluene. The presence of the hydride was confirmed by FT-IR and proton NMR spectroscopy. To the dry hydride, 6-bromo-1-hexene (100 µl, 123 mg, 0.747 mmol) and isododecane (100 µl) as an internal standard, and 2,2-azobisisobutyronitrile (5.5 mg, ~ 6 mol %) was added in toluene. The reaction was heated at 40 ºC and samples taken periodically for analysis by gas chromatography.

Result:
The conversion of the 6-bromo-1-hexene was excellent, no detectable level remained at the end of the reaction. The selectivity was to MCP however not as good as that reported for tributyltin hydride for the radical cyclisation to MCP under similar conditions. The hydride concentration in the solid network is too high to allow time for the free radical rearrangement to take place before the next hydrogen transfer step. Essentially, R_h (rate of hydrogen transfer to the hexenyl radical) is too fast compared with R_r (rate of intra-molecular free radical rearrangement) due to the local high concentration of tin hydride inside the material. Hence, hexane is favourable formed.



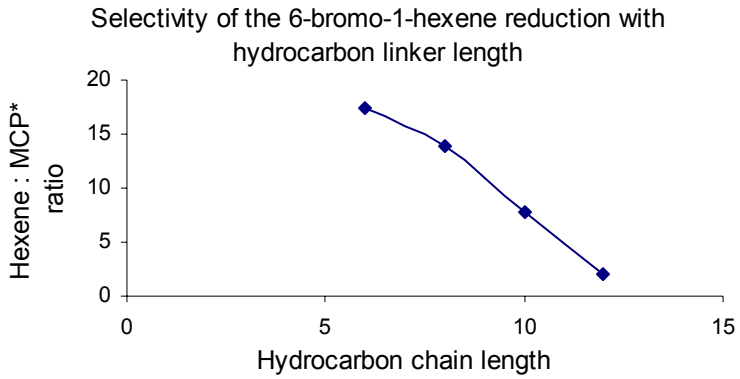
Hydrogenation of 6-bromo-1-hexene with $HSn((CH_2)_{12})_{3/2}$
Selectivity, Hexene 67.1%, methylcyclopentane 32.9%, final mass balance 96%

Experimental (Effect of chain length on the MCP selectivity)
The materials, $PhSn((CH_2)_6)_{3/2}$, $PhSn((CH_2)_8)_{3/2}$, $PhSn((CH_2)_{10})_{3/2}$ and $PhSn((CH_2)_{12})_{3/2}$ were prepared according to method C and reacted with bromine at a bromine to tin ratio of 1.00 : 1.00. 0.5 g samples of each material were brominated and reduced with $LiAlH_4$ in diethyl ether except for $BrSn((CH_2)_{12})_{3/2}$ network that was reduced with diisobutylaluminium hydride, the networks were then extensively washed in diethyl ether, ethanol, water, ethanol and finally diethyl ether again. 27 µl of 6-bromo-1-hexene, 5 ml toluene and 1.46 mg of azobis(cyclohexane carbonitrile) was added to each material and the reaction heated to 40 °C for 24 h.

Results
Effects on selectivity of the 6-bromo-1-hexene reduction of changing the catalysts hydrocarbon chain length.

Linker Between Tin Atoms	Methylcyclopentane To Hexene Ratio
$-(CH_2)_6-$	1.00 : 17.5
$-(CH_2)_8-$	1.00 : 13.9
$-(CH_2)_{10}-$	1.00 : 7.81
$-(CH_2)_{12}-$	1.00 : 2.04*

* DIBAL-H used, $LiAlH_4$ gave a ratio of 1.00 : 11.20



* MCP = Methylcyclopentane

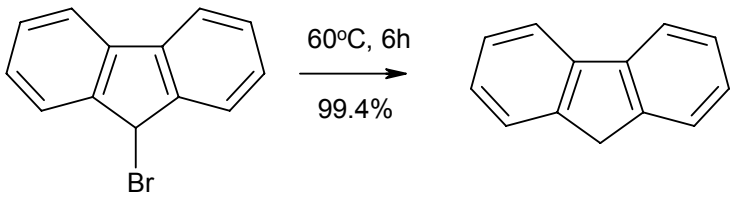
(ii) Reduction of 9-bromofluorene

Experimental

1.00 g of $PhSn((CH_2)_{12})_{3/2}$ network was treated with a 1.0 molar equivalent of bromine and then reduced with $LiAlH_4$ in diethyl ether. This was then washed with diethyl ether, ethanol, water, ethanol and diethyl ether before being heated to 100 °C under vacuum to dry the material. 0.50 g of this was used to reduce 57.1 mg of 9-bromofluorene in toluene. Azobis(cyclohexane carbonitrile) was used as the initiator (4.5 mg) and the reaction was run for 6 h at a temperature of 60 °C. At the end of the reaction the solution was collected by filtration and the toluene was removed under vacuum, the pale yellow solid was analysed by proton NMR spectroscopy. This spectrum was compared to authentic samples of fluorine and 9-bromofluorene.

Results

The integration ratio of the product and substrate for the reduction of 9-bromofluorene was 1.00:0.003, hence a molar ratio of 1.00:0.006, this is a conversion of 99.4% and this was the only product obtained. This result compares quite favourably to the reduction carried out using a polystyrene supported dibutyltin hydride in 1991, the authors of which reported a conversion of only 72 % under similar conditions. [Journal of Organic Chemistry, Volume 56, No. 21, 1991, p5971]



Reduction of 9-bromofluorene with $HSn((CH_2)_{12})_{3/2}$.

(iii) Reduction of benzaldehyde to benzyl alcohol with $HSn((CH_2)_{12})_{3/2}$.

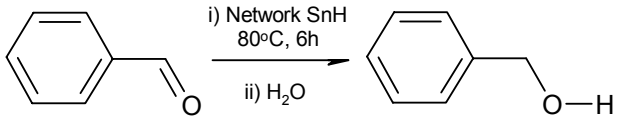
Experimental

1.00 g of $PhSn((CH_2)_{12})_{3/2}$ network was treated with a 1.0 molar equivalent of bromine and then reduced with $LiAlH_4$ in diethyl ether. This was then washed with diethyl ether, ethanol, water, ethanol and diethyl ether before being heated to 100 °C under vacuum to dry the material. 0.50 g of this was used to reduce 20 µl of benzaldehyde in toluene. Azobis(cyclohexane carbonitrile) was used as the initiator

(2.2 mg) and the reaction was run at 80 °C for 6 h. At the end of the reaction the solid was collected by filtration and washed with toluene and diethyl ether, this powdery solid was then dried under vacuum. Water was added to the solid followed by diethyl ether and the sample left overnight, this was then heated under reflux for 20 min before the solution was collected by filtration and the ether removed under vacuum. The resulting product was analysed by proton NMR spectroscopy.

Results

The proton NMR spectroscopy analysis of the reduced benzaldehyde was found to contain benzyl alcohol as the only product, although the yield was only 6.54 %, the selectivity was 100 % to benzyl alcohol.



Reduction of benzaldehyde to benzyl alcohol with $HSn((CH_2)_{12})_{3/2}$.